

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2005-085967**

(43)Date of publication of application : **31.03.2005**

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(51)Int.Cl.

**H01F 1/33**

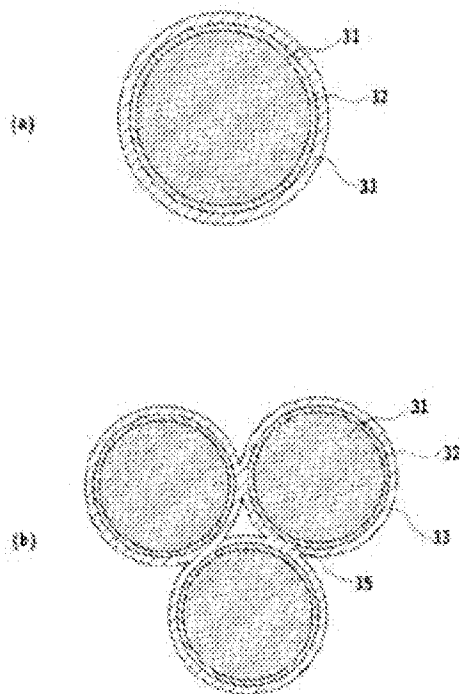
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## (54) COMPOSITE MAGNETIC PARTICLE AND COMPOSITE MAGNETIC MATERIAL



(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a composite magnetic material capable of establishing the compatibility between a high permeability and a high resistivity in a high-frequency region.

**SOLUTION:** A metallic material coating film 32 is coated on the surface of metallic magnetic particles 31, and further the surface is coated by a ferrite coating film 33 being an oxide magnetic coating film. By providing the metallic material coating film 32 between the ferrite coating film 33 and the metallic magnetic particles 31 can suppress the diffusion of oxygen from the ferrite coating film 33 to the metallic magnetic particles 31 at sintering of the composite magnetic particles, thereby avoiding reduction in the resistivity of the ferrite coating film 33 due to oxygen deficiency of the ferrite coating film 33, having conventionally been caused at sintering at

a high temperature of 400°C or over, and reduction in the insulation performance among the compound magnetic particles. Moreover, since the composite magnetic particles, after the sintering, are bonded via a ferrite bond region 35 with a wide contact area, a high permeability can be maintained.

## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to a composite magnetic material more compatible in the high magnetic permeability and high resistivity in a high frequency region in details about a composite magnetic material.

[Background of the Invention]

[0002]

In connection with the miniaturization and the weight saving of various electronic equipment in recent years, the miniaturization and the weight saving are demanded also about several kinds of parts, such as switching power supply carried in these electronic devices. In the switching power supply used for the notebook sized personal computer and small portable device with which slimming down is called for, thin CRT, or a flat-panel display, such a miniaturization and a weight saving are demanded especially strongly. However, magnetic parts which are the main component parts, such as a transformer and a reactor, occupied big volume, and the conventional switching power supply did not obtain a colander, but there was a limit in a miniaturization, a weight saving, and slimming down.

[0003]

Metal magnetic materials, such as Sendust and a permalloy, and oxide magnetic materials, such as a ferrite, were conventionally used for components for magnetic parts used for such switching power supply, such as a transformer and a reactor. While a metal magnetic material has high saturation magnetic flux density and amplitude permeability, since electrical resistivity is low, the eddy current loss especially in a high frequency band becomes large, and it becomes an obstacle to the miniaturization of the magnetic parts in recent years in which high-speed operation and a high frequency drive are called for. On the other hand, since electrical resistivity of an oxide magnetic material is high compared with a metal magnetic material, although its eddy current loss produced in a high frequency band is small, since saturation magnetic flux density is low, it is difficult to make the volume small. Also when using which magnetic material of a metal magnetic material or an oxide magnetic material as a component for magnetic parts, the volume of the magnetic substance core was a key factor which determines an inductance value, and unless the magnetic properties of the magnetic material itself were raised, a miniaturization, the weight saving, and slimming down of magnetic parts were difficult.

[0004]

These days in view of such a problem, the composite magnetic material in which the film of the high oxide magnetic material of electrical resistivity was formed on the surface of the metal magnetic particle which has high saturation magnetic flux density and amplitude permeability has come to be proposed. In such a composite magnetic material, since the fall of magnetic properties, such as amplitude permeability and saturation magnetic flux density, will arise if thickness of an oxide magnetism film is thickened too much, it is made important in the range from which the insulation between metal magnetic particles is obtained to make a film form thinly uniformly.

[0005]

For example, the high permeability magnetic material in which the film of the metallic

oxide of high magnetic permeability was formed on the surface of the metal magnetic material is proposed by the patent documents 1. The patent documents 2 has disclosed a manufacturing method that hydrostatic pressure calcination between heat is carried out after heat-treating at the temperature which does not spoil the magnetic properties of a metal magnetic material, in order to propose the high-density sintering magnetic body which covered the surface of a 1-10-micrometer metal magnetic particle with the metallic-oxide magnetic material of the spinel presentation by which the presentation notation is carried out by  $M\text{-Fe}_x\text{O}_4$  (however, M is in any of nickel, Mn, and Zn, and x is two or less) and to obtain such a high-density sintering magnetic body. The patent documents 3 has disclosed invention of the composite magnetic material which covered the surface of metal or the magnetic body particle powder of an intermetallic compound with the soft ferrite layer, carried out compression molding of this particle powder by a radio frequency heating method or plasma discharge irradiation, and formed the magnetic path between magnetic body particles via the soft ferrite layer.

[0006]

The patent documents 4 has disclosed the method of covering the soft magnetism substance of high resistance to soft magnetism metal particles, carrying out plasma activated sintering of this, and manufacturing the magnetic core made from compound soft magnetic materials.

The magnetic core obtained by this method is supposed that thickness of high resistance soft magnetism substance covering can be made into the value of a request of core loss by setting up properly.

The patent documents 5 has disclosed the method of acquiring the soft magnetism Plastic solid of high specific resistance by high density using the soft magnetism particles which consist of the metal particles of soft magnetism, high resistance material covered by that surface, and a phosphoric acid system chemical conversion film covered by the surface of this high resistance material.

[0007]

It is also possible to apply various kinds of metal alkoxides or metal salt to a composite magnetic material. For example, joining to the patent documents 6 using the solution which becomes a joint part of a magnetic ferrite and a nonmagnetic ferrite from the metal alkoxide of Ti, Zr, Ta, Fe, aluminum, and Si or metal salt of Zr in a magnetic head core is proposed.

Thereby, as compared with the manufacturing method of the conventional composite magnetic material, low temperature joining is possible, and it is supposed that junction at the temperature to which the stoma in the isostatic press processing (HIP) between heat does not return is become possible.

[0008]

The ferrite manufacture in very low temperature is attained by using a metal alkoxide. For example, in the patent documents 7, that nickel ferrite crystal is obtained by performing hydrolysis and flowing back at about 80 °C using a metal alkoxide, and carrying out temporary quenching at 400 °C and crystallizing as a ferrite at 330 °C as a result of differential thermal analysis are indicated.

[0009]

The patent documents 8 has disclosed the composite magnetic material obtained by

melting the silane monomer as nonproliferation material in a solvent, carrying out the surface treatment of the FeNi system soft magnetic powder by nonproliferation material, mixing this FeNi system soft magnetic powder and soft magnetic powder of a FeSi system alloy, a FeAl system alloy, or a FeAlSi system alloy, and fabricating and heat-treating.

[0010]

[Patent documents 1] JP,S53-91397,A

[Patent documents 2] JP,S56-38402,A

[Patent documents 3] JP,2003-86415,A

[Patent documents 4] JP,H5-47541,A

[Patent documents 5] JP,2001-85211,A

[Patent documents 6] JP,H7-130526,A

[Patent documents 7] JP,H5-299226,A

[Patent documents 8] JP,2001-015320,A

[Description of the Invention]

[Problem to be solved by the invention]

[0011]

Shaping of the metal magnetic material which has the conventional oxide magnetic material film was performed by pressure sintering by ordinary pressure sintering by compression forming, a vacuum sintering method or a reducing atmosphere sintering process, etc., a hotpress sintering process, a HIP sintering process, etc. including the method indicated to the patent documents 1 and the patent documents 2.

[0012]

Drawing 1 (a) - (c) is a figure for soft magnetism metal particles to explain the integrated state of the compound magnetic particles covered with the oxide magnetic material film, and soft magnetism metal particles and 12 are oxide magnetic material films 11 among these figures. If compression molding is performed, as shown in drawing 1 (a), contact of particles will turn into point contact for the curved surface of the compound magnetic particle surface, the magnetic combination portion of a compound magnetic particle will become extremely small, and amplitude permeability will become low. By carrying out plastic deformation of the compound magnetic particle, as shown in drawing 1 (b), it is also possible to raise amplitude permeability by enlarging the touch area of particles, but. As the oxide magnetic material film 12 becomes is easy to be destroyed at the time of the plastic deformation of a compound magnetic particle and it is shown in drawing 1 (c), The oxide magnetic material film 13 is broken through, soft magnetism metal-particles 11 comrades carry out direct contact, electrical resistivity falls, and, as a result, the evil of the eddy current loss of magnetic parts becoming large arises. Then, the technique of promoting the thermal diffusion reaction between compound magnetic particles by sintering, and combining particles by this is proposed.

[0013]

Drawing 2 is a figure for explaining the example of the contact state of the compound magnetic particles at the time of fabricating by a sinter molding method, and, as for 11, an oxide magnetic material film and 13 are the reaction parts of compound magnetic particles soft magnetism metal particles and 12 in this figure. According to the sinter molding method, as shown in this figure, it reacts without a thermal diffusion reaction's arising between [ of a compound magnetic particle ] oxide magnetic material film 12 by

sintering, and destroying the soft magnetism metal particles 11, and it becomes possible to combine particles physically, without spoiling the magnetic combination between compound magnetic particles.

[0014]

However, the temperature which such sintering takes is 900-1200 °C and an elevated temperature, and 1 hour or more are needed also for sintering time. On the other hand, by sintering at the temperature of not less than at least 500 °C, although the effect by heat treatment is accepted even if it is not completeness, the magnetic combination between particles, If it holds at the temperature over about 400 °C for 1 hour or more, oxygen in the oxide magnetic material film 12 will be spread in the soft magnetism metal-particles 11 side, and the oxide magnetic material film 12 will be returned.

If such reduction arises, electrical resistivity falls by the oxygen deficiency of the oxide magnetic material film 12, as a result eddy current loss will become large and the amplitude permeability in a high frequency region of 1 MHz or more will fall. If it performs not less than 600 °C high temperature processing, in addition to the above-mentioned oxygen deficiency, soft magnetism metal-particles 11 comrades will react in the form which breaks through the oxide magnetic material film 12 with the crystal growth of the soft magnetism metal particles 11, electrical resistivity will fall, and use in a high frequency region will become impossible.

[0015]

If a plasma activated-sintering method is used like invention indicated to the patent documents 4, It becomes possible to be able to make it sinter in a short time of a for [ about 1 to 10 minutes ] in a 600-1200 °C temperature requirement, and to reduce the oxygen diffusion from the oxide magnetic material film 12 to the soft magnetism metal particles 11. However, the reduction effect of this oxygen diffusion originates in shortening of sintering time, and has not realized prevention of oxygen diffusion and control of crystal growth structurally. For this reason, intrinsically, the same phenomenon as the case where sinter molding is performed will have arisen.

[0016]

In the case of the compound magnetic particle which becomes the patent documents 5 from the phosphoric acid system chemical conversion coat which covers the surface of soft magnetism metal particles like a description, the high resistance material which covers that surface, and this high resistance material, Since the interface of soft magnetism metal particles and high resistance material does not necessarily have a diffusion barrier layer, oxygen diffusion cannot be prevented.

[0017]

Thus, the compound magnetic particle which consists of soft magnetism metal particles covered with the oxide magnetic material film, If it sinters while amplitude permeability does not improve without sintering, without obtaining sufficient magnetic combination between particles, Oxygen in an oxide magnetic material film is spread in soft magnetism metal particles, and an oxide magnetic material film is returned, or, When soft magnetism metal particles coupled directly with the crystal growth of soft magnetism metal particles, there is a problem of causing decline in resistivity and the high magnetic permeability and high resistivity in the high frequency region were not able to be reconciled using the magnetic material which has high saturation magnetic flux density.

[0018]

The place which this invention was made in view of such a problem, and is made into the purpose, By controlling the oxygen diffusion to the soft magnetism metal particles from the oxide magnetic material film at the time of sintering, the insulation between soft magnetism particles is improved and it is in providing a composite magnetic material compatible in the high magnetic permeability and high resistivity in a high frequency region by this.

[Means for solving problem]

[0019]

In order that this invention may attain such a purpose, as for the 1st invention, the surface of the metal magnetic particle is covered with the metallic material film, and the metallic material film concerned is a compound magnetic particle covering with the oxide magnetism film.

[0020]

In the 2nd invention, said metallic material film consists of two-layer [ of the 1st and 2nd metallic material films ] in the 1st invention, It is a compound magnetic particle, wherein the surface of said metal magnetic particle is covered with said 1st metallic material film and the surface of the 1st metallic material film concerned is covered with said 2nd metallic material film.

[0021]

A metal magnetic particle in these invention consists of a permalloy, Fe, Co, or a FeCo alloy preferably. Said metallic material covering which covers the surface of a metal magnetic particle directly consists of nickel, Au, Cr, or Pd preferably, and said 2nd metallic material film consists of metal of a presentation containing Fe. Said oxide magnetism film consists of ferrites, such as NiZn, preferably.

[0022]

While the 3rd invention is the composite magnetic material which carried out press-forming stress relief heat treatment of the powder of a compound magnetic particle of this invention, neck formation of said compound magnetic particles is carried out via said oxide magnetism film and they join together physically, It is a composite magnetic material, wherein said metal magnetic particles have joined together magnetically.

[Effect of the Invention]

[0023]

The oxygen diffusion to the soft magnetism metal particles from the oxide magnetic material film at the time of sintering is controlled by this invention, and offer of a composite magnetic material compatible in the high magnetic permeability and high resistivity in a high frequency region is attained.

[Best Mode of Carrying Out the Invention]

[0024]

Below, an embodiment of the invention is described with reference to Drawings. In the following embodiments, although metal magnetic particles are permalloy particles and an oxide magnetism film mainly explains as what is a ferrite film, this should not be interpreted as being for embodiment of explanation and limiting such materials.

[Work example 1]

[0025]

It is a section schematic view of the sintered particle after making the compound magnetic particle which showed drawing 3 (a) in the section schematic view of the

compound magnetic particle of the simple substance of this example, and showed drawing 3 (a) drawing 3 (b) sinter. The compound magnetic particle of this example covers the metallic material film 32 on the surface of the metal magnetic particle 31, and covers the surface with the ferrite film 33 which is an oxide magnetism film further. By forming the metallic material film 32 between the ferrite film 33 and the metal magnetic particle 31. It makes it possible to control diffusion of oxygen from the ferrite film 33 produced at the time of sintering of a compound magnetic particle to the metal magnetic particle 31. In the former, decline in the resistivity of the ferrite film 33 resulting from the oxygen deficiency of the ferrite film 33 produced at the time of elevated-temperature sintering of not less than 400 °C and the insulating fall between compound magnetic particles are avoidable. The composite particles after sintering can maintain high amplitude permeability, in order to join together via the ferrite bond field 35 which has a big touch area, as drawing 3 (b) shows.

[0026]

Drawing 4 is a flow chart for explaining a compound magnetic particle of this example shown in drawing 3, and a manufacturing process of the sintered compact. First, the metal magnetic particle 31 is manufactured (Step S41). As a manufacturing method of the metal magnetic particle 31, although which methods, such as pulverizing method of a metallic magnetic substance, a water atomizing method, and the gaseous phase generating method in inside of inactive gas, may be used, when stability and mass production nature of particle shape are taken into consideration, a water atomizing method is desirable. As quality of a metallic magnetic material, if permalloy particles (47 permalloys and 78 permalloys), CoFe particles (Co<sub>30</sub>Fe<sub>70</sub>, Co<sub>50</sub>Fe<sub>50</sub>), Fe single particle, Co single particle, etc. are the materials which have magnetism, they are applicable. Although particle diameter is based also on construction material, it is desirable for a skin depth in a frequency band at the time of using as a magnetic component to become more than a particle radius. It is necessary to control so that sufficient volume filling factor is obtained in a sintering process which is a post process, a press operator degree, etc., and particle diameter becomes uniform.

[0027]

Next, the metallic material film 32 is covered on the surface of the metal magnetic particle 31 (Step S42). Below, the particles in the state where it was covered with the metallic material film 32 are called a primary compound magnetic particle for convenience. Any method of the wet method using dry process methods, such as vacuum deposition, CVD, and sputtering, and a chemical generation method as a coating method of a metallic material is applicable. The wet method is adopted and the chemical generating method generally called chemical plating, electroless deposition, etc. is covering in this example. Since the thickness of the metallic material film 32 influences greatly the magnetic combination which acts between compound magnetic particles, it is necessary to control it by the construction material of the metal magnetic particle 31, particle diameter or the characteristic of the ferrite film 33 which will be formed in behind, thickness, etc. in the optimal thickness. In order not to reduce the magnetic combination between the metal magnetic particles 31, a thing thin if possible is required, but this thickness is good to control thickness in 1 nm - 50 nm, when the metallic material film 32 takes into consideration playing the role of the prevention from oxygen diffusion. As a metallic material in which wet formation is possible, as for Cu, Fe, and Sn, although

there are Cu, nickel, Au, Fe, Cr, Pd, Sn, etc., since an oxygen diffusion preventive effect will become small if the metallic material itself oxidizes easily, avoiding is preferred.

[0028]

The ferrite film 33 which is an oxide magnetic material is formed in the surface of a primary compound magnetic particle following this (Step S43). Covering by this ferrite film is performed with ultrasonic excitation ferrite plating indicated to the patent documents 3. The primary compound magnetic particle obtained at Step S42 specifically  $\text{FeCl}_2$ . It is made to \*\*\*\* in the mixed water solution of  $\text{NiCl}_2$  and  $\text{ZnCl}_2$ , and pH is kept at 9.5, carrying out specified quantity supply of  $\text{NH}_4\text{OH}$  which is  $\text{NaNO}_2$  and pH control agent which are oxidizers. At this time, the temperature of a reaction solution is held at 60 \*\* with a hot bath, and an ultrasonic wave is given into reaction mixture by an ultrasonic horn with a frequency of 19.5 kHz. After carrying out prescribed period maintenance in this state, particle powder is rinsed, and in the atmosphere, at 60 \*\*, it is made to dry for 1 hour and extracts. Thereby, a NiZn ferrite film can be made to form in the surface of a primary composite particle. Below, the particles of this state are called a secondary compound magnetic particle for convenience. Thus, press forming of the obtained secondary compound magnetic particle is carried out, it is sintered, and it fabricates in desired magnetic core form.

[0029]

First, a metallic mold is filled up with a secondary compound magnetic particle, a 1 axis press performs press molding, and it is considered as a green compact (Step S44). In this state, it does not yet join together but point contact of the particles is only carried out by the particle contact portion 34.

[0030]

The obtained green compact is sintered at the temperature of about 300-900 \*\* (Step S45). The ferrite bond field 35 is formed by this sintering, and compound magnetic particles join together. Although the atmosphere may be sufficient as the atmosphere at the time of sintering, it is performed in a sufficiently big container, or controls an oxygen density so that the inside of a furnace does not become reducing atmosphere. Thus, the composite magnetic material of this invention is obtained.

[Work example 2]

[0031]

This example explains the example using Au as a metallic material film in Embodiment 1. As the metal magnetic particle 31, the permalloy particle (47 permalloy particles) with a mean particle diameter of 8 micrometers produced with the water atomizing method was used.

[0032]

First, the dilute-hydrochloric-acid processing and dilute-sulfuric-acid processing which are pretreatment of film formation were performed to permalloy particles, and it was immersed in the pretreatment liquid which uses a palladium chloride (0.1g/(l.)) and chloride (it is 2ml/l. about 35vol%) as the main ingredients for the nucleation of chemical plating for 1 minute. Next, it is \*\*\*\*\* during 1 minute, holding and stirring the chemical-plating liquid (pH 7) of Au which used golden potassium cyanide, sodium acid citrate, ammonium chloride, and sodium hypophosphite as the main ingredients in temperature of 60 \*\*. In order that this chemical-plating liquid might not thicken thickness of the metallic material film 32, it lowered solution temperature to 60 \*\*, and



although it is usually used at about 90 \*\*, it controlled it so that the thickness of Au coating was set to about 5 nm.

[0033]

The ferrite film 33 is formed by the procedure explained in Embodiment 1 following this. It is \*\*\*\*\* during 60 minutes, giving an ultrasonic wave to a ferrite plating solution (mixed water solution of  $\text{FeCl}_2$ ,  $\text{NiCl}_2$ , and  $\text{ZnCl}_2$ ) in this example. Rinsing and desiccation are performed after this processing, and the compound magnetic particle with which Au coating and a ferrite film covered permalloy particles doubly is formed.

[0034]

The metallic mold was filled up with about 1 g of this compound magnetic particle, and the sintering reaction of the green compact obtained by carrying out 1 axis press forming by the pressure of  $10 \text{ ton/cm}^2$  was carried out with the electric furnace of atmospheric air for 5 minutes at the sintering temperature 200 and 400 or each temperature of 600 \*\*. Thus, the core (volume <sup>3</sup> of 0.13 cm) of the ring type (the outer diameter of 8 mm, inside diameter  $\phi 3\text{mm}$ , and 3 mm in thickness) was produced.

[0035]

When the section of this core is observed with a transmission electron microscope (TEM), the contact state of the ferrite film of a compound magnetic particle is a point contact state (state equivalent to drawing 1 (a)) in having no sintering and 200 \*\* sintering.

By 400 \*\* sintering, it had changed into the state which is combined so that ferrite film 33 comrades may be narrow, as shown in drawing 3 (b) and which shows neck formation by 600 \*\* sintering to having been in the field contact state (state equivalent to drawing 1 (b)) slightly.

That is, while neck formation of the compound magnetic particles is carried out via the oxide magnetism film slack ferrite film 33 and they join together physically, permalloy particle 31 comrades which are metal magnetic particles have joined together magnetically. The ferrite film 33 was broken through and, as for most of a direct reaction and a united part, permalloy 31 comrades were not checked.

[Work example 3]

[0036]

This example explains the example using Pd as a metallic material film in Embodiment 1. The permalloy particles 31 were immersed in the processing fluid which uses a palladium chloride (0.1g/(l.)) and chloride (it is 2ml/l. about 35vol%) as the main ingredients for 5 minutes, and Pd film was formed in the surface of the permalloy particles 31. Then, ferrite film 33 formation was carried out, without making it dry. The \*\*\*\* time to a ferrite plating solution is 60 minutes like Embodiment 2. Rinsing and desiccation are performed after this processing and the compound magnetic particle with which Pd film and the ferrite film covered permalloy particles doubly is formed.

[0037]

The metallic mold was filled up with about 1 g of this compound magnetic particle, and the sintering reaction of the green compact obtained by carrying out 1 axis press forming by the pressure of  $10 \text{ ton/cm}^2$  was carried out with the electric furnace of atmospheric air for 5 minutes at the sintering temperature 200 and 400 or each temperature of 600 \*\*. Thus, the core (volume <sup>3</sup> of 0.13 cm) of the ring type (the outer diameter of 8 mm, inside diameter  $\phi 3\text{mm}$ , and 3 mm in thickness) was produced.

The section shape voice of these cores was the same as the state where Embodiment 2 explained.

[Work example 4]

[0038]

Although the metallic material which does not have magnetism was used as an oxygen diffusion preventing film in Embodiment 2 and Embodiment 3 which were mentioned above, it is more convenient for an oxygen diffusion preventing film to also have magnetism, in order not to reduce the magnetic combination between particles. There are nickel and Cr (antiferromagnet) as a metallic material which fitted the purpose of this invention and is tinged with magnetism. So, in this example, we decided to use nickel as a metallic material. Since the difference with the manufacturing process explained in Embodiment 2 is only a formation process of the metallic material film 32, below, it explains only the formation process of a Ni coat.

[0039]

As pretreatment for Ni-coat formation, dilute-hydrochloric-acid processing and dilute-sulfuric-acid processing were performed like Embodiment 2. Although what is necessary is just to carry out nucleation processing for chemical plating if needed, it is not performing in this example.

[0040]

The chemical-plating liquid (pH 4.5) of nickel which used nickel sulfate, sodium hypophosphite, and lactic acid as the main ingredients was maintained at the temperature of 50 °C following these pretreatments, and the permalloy particles 31 were immersed for 1 minute, stirring this chemical-plating liquid. Like formation of Au coating, in order not to thicken coating thickness, solution temperature is low set to 50 °C, and the thickness of nickel is controlled to about 5 nm. After this Ni-coat formation carried out ferrite film formation, without drying particles. The Reason for not establishing a drying stage is for preventing oxidation of nickel produced because particles dry. \*\*\*\*\* is 60 minutes like Embodiment 2 and Embodiment 3 at a ferrite plating solution. The compound magnetic particle with which the Ni coat and the ferrite film covered permalloy particles doubly is formed through rinsing and a drying stage after this processing.

[0041]

The metallic mold was filled up with about 1 g of this compound magnetic particle, and the sintering reaction of the green compact obtained by carrying out 1 axis press forming by the pressure of 10 ton/cm<sup>2</sup> was carried out with the electric furnace of atmospheric air for 5 minutes at the sintering temperature 200 and 400 or each temperature of 600 °C. Thus, the core (volume of 0.13 cm<sup>3</sup>) of the ring type (the outer diameter of 8 mm, inside diameter phi3mm, and 3 mm in thickness) was produced.

Section shape voice of these cores was the same as the state where Embodiment 2 explained.

[0042]

[The comparative example 1]

Only the ferrite film 33 was formed on the permalloy particle 31 surface, without forming the metallic material film 32 used as an oxygen diffusion preventing film as a comparative example. Permalloy particles and the ferrite film 33 are the same as that of what was explained in Embodiments 1-3, and conditions of press forming and sintering

of them are the same as that of an embodiment.

[0043]

When TEM observation of the section of an obtained core was carried out, it was checked that neck formation of the metal magnetic particles which a ferrite bond field is in the same state as a mimetic diagram of drawing 2, and were covered with a ferrite film is carried out. The ferrite film 33 was broken through and, as for most of a direct reaction and a united part, permalloy particle 31 comrades were not accepted.

[0044]

Drawing 5 is a figure for explaining a result of having twisted a conductor wire by which pre-insulation was carried out to a ring type core obtained by Embodiments 2-4 and the comparative example 1, having produced an inductor, and having measured relative permeability  $\mu$  in frequency of 1 MHz using a B-H analyzer of exchange. In a core fabricated by a compound magnetic particle of the comparative example 1 which did not form the metallic material film 32, so that clearly from a measurement result shown in this figure. To relative permeability falling as heat treatment temperature becomes high, each core fabricated by a compound magnetic particle of this invention which formed the metallic material film 32 shows high relative permeability as heat treatment temperature becomes high. Decline in such relative permeability is for a magnetic field to a direction which negates a magnetic field by generating of an eddy current to occur. By forming the metallic material film 32, oxygen diffusion in a high temperature region is controlled, and a result shown in drawing 5 means that low-loss magnetic parts can be obtained also in a high frequency region.

[Work example 5]

[0045]

In Embodiments 1-4 described so far, the metallic material film 32 should be covered for the composition of the compound magnetic particle of this example on the surface of the metal magnetic particle 31, and the surface should be further covered with the ferrite film 33. On the other hand, in the embodiment of the following containing this example, While the metallic material film 32 is made two-layer and the 1st metallic material film 32a realizes prevention from oxygen diffusion, it is supposed that the crystallinity of the ferrite film 33 will be improved using "covering power" at the time of plating the ferrite film 33 by the 2nd metallic material film 32b as good. "Covering power" means the homogeneity of film formation and here with "covering power is good." As a result of realizing uniform film formation, the crystallinity of the obtained film means a high thing and the crystallinity of the film formed conversely without making as uniform film formation as "covering power is bad" means a low thing.

[0046]

It is a section schematic view of the sintered particle after making the compound magnetic particle which showed drawing 6 (a) in the section schematic view of the compound magnetic particle of the simple substance of this example, and showed drawing 6 (a) drawing 6 (b) sinter. The compound magnetic particle of this example covers the 1st metallic material film 32a and the 2nd metallic material film 32b on the surface of the metal magnetic particle 31, and covers the surface with the ferrite film 33 further.

[0047]

By forming the 1st metallic material film 32a between the ferrite film 33 and the metal

magnetic particle 31. It makes it possible to control diffusion of oxygen from the ferrite film 33 produced at the time of sintering of a compound magnetic particle to the metal magnetic particle 31, In the former, decline in the resistivity of the ferrite film 33 resulting from the oxygen deficiency of the ferrite film 33 produced at the time of elevated-temperature sintering of not less than 400 °C and the insulating fall between compound magnetic particles are avoidable. The composite particles after sintering can maintain high amplitude permeability, in order to join together via the ferrite bond field 35 which has a big touch area, as drawing 6 (b) shows. The "covering power" at the time of plating the ferrite film 33 becomes possible [ improving the crystallinity of the ferrite film 33 formed by becoming good ] by covering the surface of the 1st metallic material film 32a with the 2nd metallic material film 32b.

[0048]

Drawing 7 is a flow chart for explaining the compound magnetic particle of this example shown in drawing 6, and the manufacturing process of the sintered compact. First, the metal magnetic particle 31 is manufactured (Step S71). As a manufacturing method of the metal magnetic particle 31, although which methods, such as pulverizing method of a metallic magnetic substance, a water atomizing method, and the gaseous phase generating method in the inside of inactive gas, may be used, when the stability and mass production nature of particle shape are taken into consideration, a water atomizing method is desirable. As quality of a metallic magnetic material, if permalloy particles (47 permalloys and 78 permalloys), CoFe particles (Co<sub>30</sub>Fe<sub>70</sub>, Co<sub>50</sub>Fe<sub>50</sub>), Fe single particle, Co single particle, etc. are the materials which have magnetism, they are applicable. Although particle diameter is based also on construction material, it is desirable for the skin depth in the frequency band at the time of using as a magnetic component to become more than a particle radius. It is necessary to control so that sufficient volume filling factor is obtained in the sintering process which is a post process, a press operator degree, etc., and particle diameter becomes uniform.

[0049]

Next, the 1st metallic material film 32a and the 2nd metallic material film 32b are covered on the surface of the metal magnetic particle 31 (Step S72). Below, the particles in the state where it was covered with the metallic material film 32 which consists of a metallic material film (32a and 32b) two-layer [ these ] are called a primary compound magnetic particle for convenience. Any method of the wet method using dry process methods, such as vacuum deposition, CVD, and sputtering, and a chemical generation method as a coating method of a metallic material is applicable. The wet method is adopted and the chemical generating method generally called chemical plating, electroless deposition, etc. is covering in this example. Since the thickness of the metallic material film 32 influences greatly the magnetic combination which acts between compound magnetic particles, it is necessary to control it by the construction material of the metal magnetic particle 31, particle diameter or the characteristic of the ferrite film 33 which will be formed in behind, thickness, etc. in the optimal thickness. In order not to reduce the magnetic combination between the metal magnetic particles 31, a thing thin if possible is required, but this thickness is good to control thickness in 1 nm - 50 nm, when the metallic material film 32 takes into consideration playing the role of the prevention from oxygen diffusion.

[0050]

As a metallic material in which wet formation is possible, as for using Cu, Fe, and Sn as construction material of the 1st metallic material film 32a, although there are Cu, nickel, Au, Fe, Cr, Pd, Sn, etc., since an oxygen diffusion preventive effect will become small if the metallic material itself oxidizes easily, avoiding is preferred. It is preferred to consider it as the material which improves "covering power" at the time of ferrite film 33 formation is chosen as the 2nd metallic material film 32b on the other hand, and contains Fe, and "covering power" can be most raised by considering it as Fe simple substance.

[0051]

It is thought that the Reason with preferred the 2nd metallic material film 32b containing Fe is because plating advances at the OH radical which exists in the base (namely, surface of the 2nd metallic material film 32b) plated as a reaction mechanism of ferrite plating, and a ferrite reacting. On the surface of Fe, many OH radicals exist comparatively, and a ferrite grows on this OH radical. Since many OH radicals exist on the surface of a ferrite, a ferrite grows on this OH radical. A ferrite film will be formed of a repetition of such a reaction. Therefore, if the 2nd metallic material film 32b is formed with the material of the presentation containing Fe, A ferrite film will begin to be attached, a ferrite will adhere to the 2nd metallic material film 32b surface uniformly in a stage, "covering power" will become good, and, as a result, the crystallinity of the ferrite film 33 obtained will also become high.

[0052]

The ferrite film 33 which is an oxide magnetic material is formed in the surface of a primary compound magnetic particle following this (Step S73). Covering by this ferrite film is performed with ultrasonic excitation ferrite plating indicated to the patent documents 3. The primary compound magnetic particle obtained at Step S72 specifically  $\text{FeCl}_2$ , It is made to \*\*\*\* in the mixed water solution of  $\text{NiCl}_2$  and  $\text{ZnCl}_2$ , and pH is kept at 9.5, carrying out specified quantity supply of  $\text{NH}_4\text{OH}$  which is  $\text{NaNO}_2$  and pH control agent which are oxidizers. At this time, the temperature of a reaction solution is held at 60 \*\* with a hot bath, and an ultrasonic wave is given into reaction mixture by an ultrasonic horn with a frequency of 19.5 kHz. After carrying out prescribed period maintenance in this state, particle powder is rinsed, and in the atmosphere, at 60 \*\*, it is made to dry for 1 hour and extracts. Thereby, a NiZn ferrite film can be made to form in the surface of a primary composite particle. Below, the particles of this state are called a secondary compound magnetic particle for convenience. Thus, press forming of the obtained secondary compound magnetic particle is carried out, it is sintered, and it fabricates in desired magnetic core form.

[0053]

First, a metallic mold is filled up with a secondary compound magnetic particle, a 1 axis press performs press molding, and it is considered as a green compact (Step S74). In this state, it does not yet join together but point contact of the particles is only carried out by the particle contact portion 34.

[0054]

The obtained green compact is sintered at the temperature of about 300-900 \*\* (Step S75). The ferrite bond field 35 is formed by this sintering, and compound magnetic particles join together. Although the atmosphere may be sufficient as the atmosphere at the time of sintering, it is performed in a sufficiently big container, or controls an oxygen

density so that the inside of a furnace does not become reducing atmosphere. Thus, the composite magnetic material of this invention is obtained.

[Work example 6]

[0055]

This example explains the example using Pd as the 1st metallic material film 32a in Embodiment 5. As the metal magnetic particle 31, the permalloy particle (47 permalloy particles) with a mean particle diameter of 8 micrometers produced with the water atomizing method was used.

[0056]

First, the dilute-hydrochloric-acid processing and dilute-sulfuric-acid processing which are pretreatment of film formation were performed to permalloy particles, and it was immersed in the pretreatment liquid which uses a palladium chloride (0.1g/(l.)) and chloride (it is 2ml/l. about 35vol%) as the main ingredients for the nucleation of chemical plating for 5 minutes.

[0057]

Then, the 2nd metallic material film 32b was formed continuously, without making it dry. It was immersed specifically stirring for 1 minute in the chemical-plating liquid (pH 9) of Fe which makes the particles after the 2nd metallic material film 32b formation ferrous sulfate and the Rosell salt, and uses sodium hypophosphite as the main ingredients and which was maintained at the temperature of 700 \*\*. In order that this chemical-plating liquid might not make a film thick more than needed, it lowered solution temperature to 700 \*\*, and although it is usually used at the temperature of about 900 \*\*, it controlled it so that the thickness of Fe film was set to about 1 nm.

[0058]

The ferrite film 33 is formed by the procedure explained in Embodiment 5 following this. It is \*\*\*\*\* during 60 minutes, giving an ultrasonic wave to a ferrite plating solution (mixed water solution of  $\text{FeCl}_2$ ,  $\text{NiCl}_2$ , and  $\text{ZnCl}_2$ ) in this example. Rinsing and desiccation are performed after this processing, and the compound magnetic particle with which Pd film, Fe film, and the ferrite film covered permalloy particles is formed.

[0059]

The metallic mold was filled up with about 1 g of this compound magnetic particle, and the sintering reaction of the green compact obtained by carrying out 1 axis press forming by the pressure of  $10 \text{ ton/cm}^2$  was carried out with the electric furnace of atmospheric air for 5 minutes at the sintering temperature 200 and 400 or each temperature of 600 \*\*. Thus, the core (volume <sup>3</sup> of 0.13 cm) of the ring type (the outer diameter of 8 mm, inside diameter  $\phi 3\text{mm}$ , and 3 mm in thickness) was produced.

[0060]

When the section of this core is observed with a transmission electron microscope (TEM), the contact state of the ferrite film of a compound magnetic particle is a point contact state (state equivalent to drawing 1 (a)) in having no sintering and 200 \*\* sintering.

By 400 \*\* sintering, it had changed into the state which shows neck formation as shown in drawing 3 (b) by 600 \*\* sintering to having been in the field contact state (state equivalent to drawing 1 (b)) slightly.

The ferrite film 33 was broken through and, as for most of a direct reaction and a united part, metal magnetic particle 31 comrades were not checked. It was checked by having

formed the 2nd metallic material film 32b that the high crystalline ferrite film 33 is obtained.

[Work example 7]

[0061]

Although the metallic material which does not have magnetism was used as an oxygen diffusion preventing film in Embodiment 6 mentioned above, it is more convenient for an oxygen diffusion preventing film to also have magnetism, in order not to reduce the magnetic combination between particles. There are nickel and Cr as a metallic material which fitted the purpose of this invention and is tinged with magnetism. So, in this example, we decided to use nickel as a metallic material. Since the difference with the manufacturing process explained in Embodiment 6 is only a formation process of the 1st metallic material film 32a, below, it explains only the formation process of a Ni coat.

[0062]

As pretreatment for Ni-coat formation, dilute-hydrochloric-acid processing and dilute-sulfuric-acid processing were performed like Embodiment 6. Although what is necessary is just to carry out nucleation processing for chemical plating if needed, it is not performing in this example.

[0063]

The chemical-plating liquid (pH 4.5) of nickel which used nickel sulfate, sodium hypophosphite, and lactic acid as the main ingredients was maintained at the temperature of 50 °C following these pretreatments, and the permalloy particles 31 were immersed for 1 minute, stirring this chemical-plating liquid. Like formation of Au coating, in order not to thicken coating thickness, solution temperature is low set to 50 °C, and the thickness of nickel is controlled to about 10 nm. After this Ni-coat formation carried out 2nd metallic material film 32b and ferrite film 33 formation, without drying particles. The Reason for not establishing a drying stage is for preventing oxidation of nickel produced because particles dry. Thus, the compound magnetic particle with which the Ni coat, Fe film, and the ferrite film covered permalloy particles is formed.

[0064]

The metallic mold was filled up with about 1 g of this compound magnetic particle, and the sintering reaction of the green compact obtained by carrying out 1 axis press forming by the pressure of 10 ton/cm<sup>2</sup> was carried out with the electric furnace of atmospheric air for 5 minutes at the sintering temperature 200 and 400 or each temperature of 600 °C. Thus, the core (volume <sup>3</sup> of 0.13 cm) of the ring type (the outer diameter of 8 mm, inside diameter phi3mm, and 3 mm in thickness) was produced. The section shape voice of these cores was the same as the state where Embodiment 6 explained.

[0065]

Drawing 8 twists the conductor wire by which pre-insulation was carried out to the ring type core obtained in Embodiment 6 and Embodiment 7, and produces an inductor, The figure for explaining the result of having measured relative permeability  $\mu_r$  in the frequency of 1 MHz using the B-H analyzer of exchange has also shown simultaneously the measurement result about the core obtained by the comparative example 1 for comparison. In the core fabricated by the compound magnetic particle of the comparative example 1 which did not form the metallic material film 32, so that clearly from the measurement result shown in this figure. To relative permeability falling as heat treatment temperature becomes high, each core fabricated by the compound magnetic

particle of this invention which formed the metallic material film 32 shows high relative permeability as heat treatment temperature becomes high. The decline in such relative permeability is for the magnetic field to the direction which negates a magnetic field by generating of an eddy current to occur. By forming the metallic material film 32, the oxygen diffusion in a high temperature region is controlled, and the result shown in drawing 8 means that low-loss magnetic parts can be obtained also in a high frequency region, as drawing 5 explained.

[0066]

Drawing 9 is a figure for explaining the result of having measured relative permeability  $\mu$  in the frequency of 5 MHz of the ring core obtained in Embodiment 7 and Embodiment 4. Embodiment 4 is an embodiment in case the metal film 32 is nickel monolayer, and Embodiment 7 is an embodiment at the time of using double structure of nickel and Fe. It turns out that the high frequency characteristic of the ring core of Embodiment 7 made into the double structure of nickel and Fe is far excellent in the metal film 32 as compared with the characteristic of the ring core of Embodiment 4 of nickel monolayer so that clearly from this figure. This result by doubling a metallic material film and raising the crystallinity of a ferrite film, By the insulation between permalloy particle 31 improving and avoiding the fall of the electrical resistance of magnetic parts, it is because it is possible for there to be no fall of relative permeability  $\mu$  and to improve a high frequency characteristic even in a high frequency region.

[0067]

Although the compound magnetic particle was made into the usual thing to do for a glass burn join in old Embodiments 1-7, if plasma activated sintering etc. are used, the effect of this invention called high-magnetic-permeability-izing and high-resistivity-izing will become still larger. If it supposes that a metal alkoxide is added and sintered in order to promote neck formation, it will become possible [ neck formation ] also for low temperature sintering.

[Industrial applicability]

[0068]

This invention enables offer of a composite magnetic material compatible in the high magnetic permeability and high resistivity in a high frequency region.

[Brief Description of the Drawings]

[0069]

[Drawing 1] It is a figure for soft magnetism metal particles to explain the integrated state of the compound magnetic particles covered with the oxide magnetic material film.

[Drawing 2] It is a figure for explaining the example of the contact state of the compound magnetic particles at the time of fabricating by a sinter molding method.

[Drawing 3] It is a figure for explaining the situation of the compound magnetic particle of Embodiment 1, and is a section schematic view of the sintered particle after (a) sinters the section schematic view of the compound magnetic particle of a simple substance and (b) made the compound magnetic particle sinter.

[Drawing 4] It is a flow chart for explaining the compound magnetic particle of Embodiment 1 shown in drawing 3, and the manufacturing process of the sintered compact.

[Drawing 5] It is a figure for explaining the result of having twisted the conductor wire by which pre-insulation was carried out to the ring type core obtained by Embodiments 2-4



and the comparative example 1, having produced the inductor, and having measured relative permeability  $\mu$  in the frequency of 1 MHz using the B-H analyzer of exchange.

[Drawing 6] It is a figure for explaining the situation of the compound magnetic particle of Embodiment 5, and is a section schematic view of the sintered particle after (a) sinters the section schematic view of the compound magnetic particle of a simple substance and (b) made the compound magnetic particle sinter.

[Drawing 7] It is a flow chart for explaining the compound magnetic particle of Embodiment 5 shown in drawing 6, and the manufacturing process of the sintered compact.

[Drawing 8] It is a figure for explaining the result of having twisted the conductor wire by which pre-insulation was carried out to the ring type core obtained in Embodiment 6 and Embodiment 7, having produced the inductor, and having measured relative permeability  $\mu$  in the frequency of 1 MHz using the B-H analyzer of exchange.

[Drawing 9] It is a figure for explaining the result of having measured relative permeability  $\mu$  in the frequency of 5 MHz of the ring core obtained in Embodiment 7 and Embodiment 4.

[Explanations of letters or numerals]

[0070]

11 Soft magnetism metal particles

12 Oxide magnetic material film

13 The reaction part of compound magnetic particles

31 Metal magnetic particle

32 Metallic material film

32a The 1st metallic material film

32b The 2nd metallic material film

33 Ferrite film

34 Particle contact portion

35 Ferrite bond field

## CLAIMS

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[Claim(s)]

[Claim 1]

A compound magnetic particle, wherein the surface of a metal magnetic particle is covered with a metallic material film and the metallic material film concerned is covered with an oxide magnetism film.

[Claim 2]

The compound magnetic particle according to claim 1, wherein said metallic material film consists of two-layer [ of the 1st and 2nd metallic material films ], the surface of said metal magnetic particle is covered with said 1st metallic material film and the surface of the 1st metallic material film concerned is covered with said 2nd metallic material film.

[Claim 3]

The compound magnetic particle according to claim 1 or 2, wherein said metal magnetic

particle consists of a permalloy, Fe, Co, or a FeCo alloy.

[Claim 4]

The compound magnetic particle according to any one of claims 1 to 3, wherein said metallic material covering which covers the surface of said metal magnetic particle directly consists of nickel, Au, Cr, or Pd.

[Claim 5]

The compound magnetic particle according to any one of claims 1 to 4, wherein said 2nd metallic material film consists of metal of a presentation containing Fe.

[Claim 6]

The compound magnetic particle according to any one of claims 1 to 5, wherein said oxide magnetism film consists of ferrites.

[Claim 7]

The compound magnetic particle according to claim 6, wherein said ferrite is a NiZn ferrite.

[Claim 8]

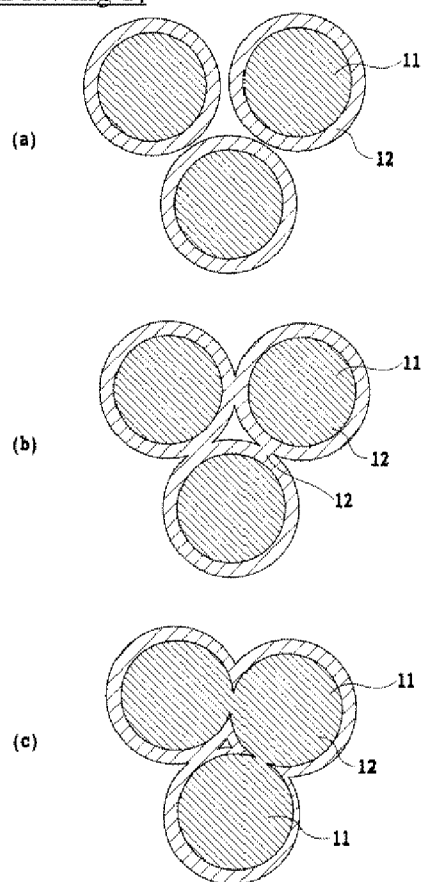
It is the composite magnetic material which carried out press-forming stress relief heat treatment of the powder of the compound magnetic particle according to any one of claims 1 to 7,

A composite magnetic material characterized by said metal magnetic particles having joined together magnetically while neck formation of said compound magnetic particles is carried out via said oxide magnetism film and they join together physically.

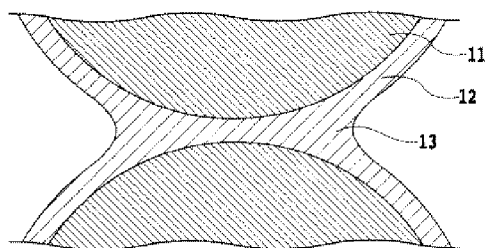
## **DRAWINGS**

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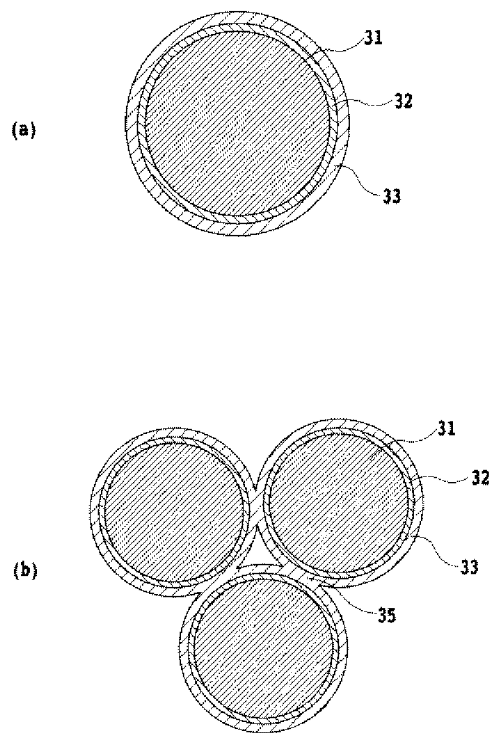
[Drawing 1]



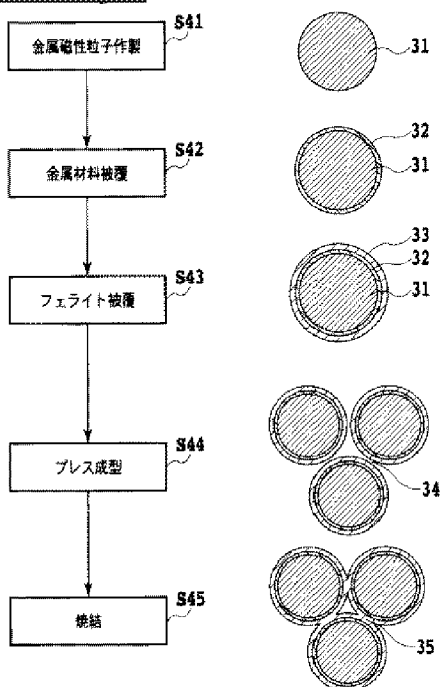
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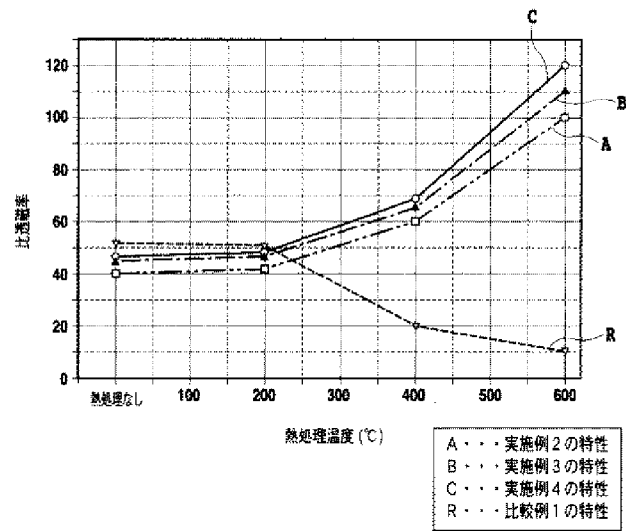
[Drawing 3]



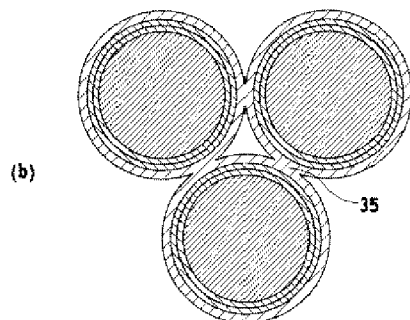
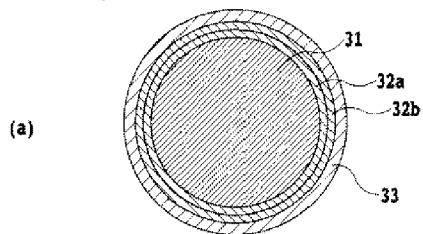
[Drawing 4]



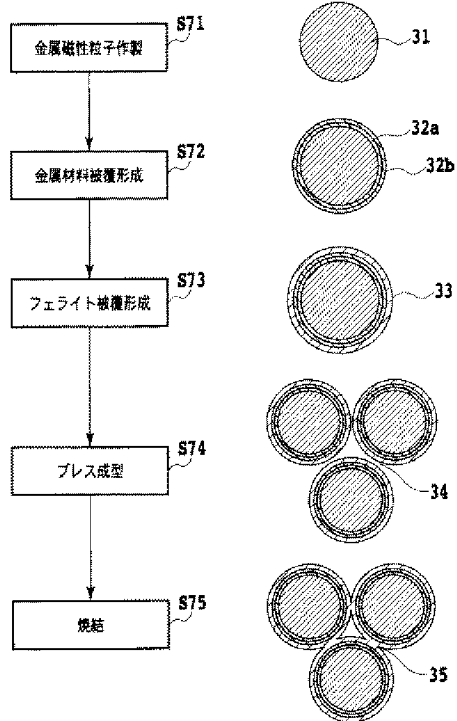
[Drawing 5]



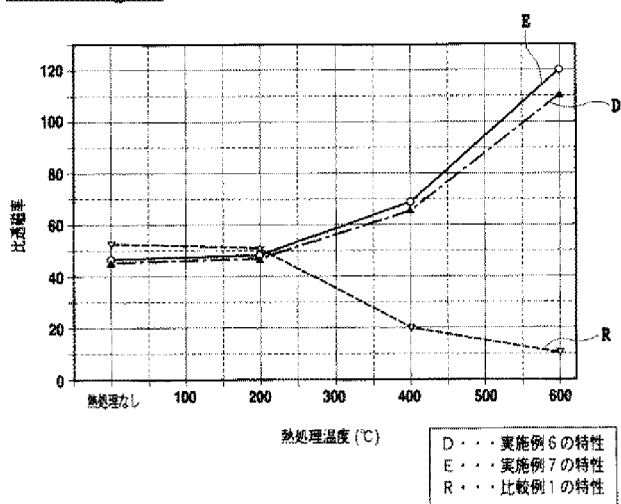
[Drawing 6]



[Drawing 7]



[Drawing 8]



[Drawing 9]

